[12080/46001]

Erratum Patent: 8204034

Publication no. 2469134

International Classification: 3

A 24 D 3/16, ¾

Erratum

The filing date is incorrect for item 22 on the cover page of the patent application.

In place of: November 12, 198<u>9</u>

It should read: November 12, 198<u>0</u>.

IMPROVEMENT TO FILTERS OR FILTRATION MATERIALS FOR TOBACCO SMOKE

[Perfectionnement aux filtres ou aux matériaux de filtration de la fumée de tabac]

David Allan Matkin

PUBLICATION COUNTRY	(10): FR
DOCUMENT NUMBER	(11): 2469134
DOCUMENT KIND	(12): PATENT APPLICATION
	(13):
PUBLICATION DATE	(43):
PUBLICATION DATE	(45):
DATE OF PUBLIC AVAILABILITY OF APPLICATION	(41) BOPI, Lists, no. 21, May 22, 1981
APPLICATION NUMBER	(21): 8024034
APPLICATION DATE	(22): 19801112
ADDITION TO	(61):
INTERNATIONAL CLASSIFICATION	(51): A 24 D 3/16, 3/04
DOMESTIC CLASSIFICATION	(52):
PRIORITY COUNTRY	(33): Great Britain
PRIORITY NUMBER	(31): 7939185, 8019460
PRIORITY DATE	(32): November 13, 1979 June 13, 1980
INVENTOR	(72): David Allan Matkin
APPLICANT	(71): BRITISH-AMERICAN TOBACCO COMPANY LIMITED, residing in Great Britain
PATENTEE	(73): same as 71
ATTORNEY OR AGENT	(74): Cabinet technique Ch. Assi et L. Genès 41, rue des Martyrs, 75009 Paris, France
TITLE	(54): IMPROVEMENT TO FILTERS OR FILTRATION MATERIALS FOR TOBACCO SMOKE
FOREIGN TITLE	[54A]: Perfectionnement aux filtres ou aux matériaux de filtration de la fumée de tabac

The invention relates to improvements to filters or filtration materials for tobacco smoke.

An object of the invention is the realization of a filter or filtration material to eliminate nitric oxide (hereinafter, simply referred to as "NO") from a gaseous environment, for example, air.

A particular object of the invention is the realization of a filter or filtration material that is effective in practice in eliminating the NO contained in cigarette smoke or other smoking articles.

According to the invention, a filter or filtration material to eliminate nitric oxide comprises an activated carbon on which has been adsorbed a C-nitroso compound, one (or more) substituent group or groups on this compound, other than the nitroso group or groups, having an identity and position in the molecular structure of the compound such that it has no adverse or dangerously harmful effect on the integrity of the nitroso group or groups.

Preferably, the C-nitroso compound is an aromatic compound.

The activated carbon can have a fibrous, filamentous, or cloth form, but is preferably in particulate form and is preferably a granular carbon extracted from coal. The carbon must be porous so that the total surface area is relatively large. The particle size can advantageously be in the range of 5 to 50 and preferably in the range of 12 to 30 using a British standard sieve gauge. The carbon can be bonded, at least loosely, in a state that enables the smoke to have access to the carbon.

The loading of the C-nitroso compound on the carbon is suitably on the order of 2 to 15% by weight on an untreated carbon basis, and preferably 5 to 7%.

Whereas a filter effective to remove at least 30 to 35% by weight of NO contained in tobacco smoke is generally considered useful, a less efficient NO filtration efficiency, for example, on the order of approximately 20%, could be considered to have a certain utility.

The use in a filter of a C-nitroso compound adsorbed on activated carbon can be combined with filter ventilation, a synergistic effect being apparently obtainable. Consequently, in some cases, an overall filter efficiency for NO can be obtained in a way that is both practically and economically convenient by using the aforementioned combination.

The NO filtration efficiency can also be significantly enhanced by using an activated carbon that has been loaded with a suitable metal. To obtain the best results, the metal should be in the metallic form, that is, have zero atomicity. This metal can be copper or iron at a loading level on an untreated carbon basis as high as approximately 10%. The loading of the metal can advantageously be comprised between 1 and 5%. Not only can the NO filtration efficiencies in the range that can be obtained with unmetallized

carbon be obtained at very reduced loading levels of the C-nitroso compound by metallizing the carbon, but even at low metal loading levels, we can obtain NO filtration values that appreciably exceed those we can obtain using unmetallized carbon. Thus with metallized carbon, the loading of the C-nitroso compound can be comprised between approximately 2% and approximately 5% on an untreated carbon basis.

Metallization of the carbon also has the advantage that the filtration material is thereby made effective for eliminating a component of tobacco smoke in addition to NO, for example, hydrocyanic acid.

EXAMPLE 1

Nitrosobenzene was prepared using the method of Coleman et al. (Organic Syntheses Collective, vol. III, ed. E. C. Horning, pp. 668-670) and a quantity of activated granular carbon, sold under the Anthrasorb CC 1236 trade name by Cardian Chemical Co. of Cheltenham (England), was completely wetted with a solution of nitrobenzene in ethanol. The solvent was left to evaporate at room temperature. The corresponding loading level of the adsorbed nitrosobenzene was 7%.

Then, 100 mg of the thus treated granular carbon was arranged in the cavity of a triple filter comprising, at each end of the cavity, a 5 mm long cellulose acetate plug. The filter was attached to a cigarette rod filled with properly heat cured tobacco. The filter cigarette thus formed was then smoked under standard conditions, that is, using 35 cm^3 puffs of 2 second duration every minute, until an 8 mm long stub was obtained. It was found that the filter eliminated 63% by weight of the NO contained in the tobacco smoke.

EXAMPLE II

Experiment I was repeated using 2-nitrosobenzene, sold by Aldrich Chemical Co. Ltd., of Gillingham, Dorset (England), at the same loading level, in place of nitrosobenzene. The observed NO filtration efficiency was 50%.

EXAMPLE III

2, 4, 6-trimethylnitrosobenzene was prepared by the method of Di Nunno (Journal of the Chemical Society (Section C), 1970, p. 1423). The process of example I was repeated, using the compound thus prepared. The observed NO filtration efficiency was 40%.

EXAMPLE IV

Example I was repeated using 2, 4, 6-tri-t-butylnitrosobenzene prepared from 2, 4, 6-tri-t-butylaniline using the method of Di Nunno, the intermediate compound being prepared by the method of Bartlett (Journal of the American Chemical Society, 1956, vol. 76, p. 2349). The observed NO filtration efficiency was 65%.

EXAMPLE V

4-chloronitrosobenzene was prepared from 4-chloroaniline using the method of Di Nunno, and example I was repeated. The observed NO filtration efficiency was 62%.

EXAMPLE VI

Example I was repeated, but the C-nitroso compound was replaced with the 2, 4, 6-trichloronitrosobenzene obtained by the method of Di Nunno, the crude product having been recrystallized twice with glacial acetic acid. The observed NO filtration efficiency was 38%.

EXAMPLE VII

Example 1 was repeated, using 2-methyl-2-nitrosopropane, sold by Aldrich Chemical Co. Ltd. The observed NO filtration efficiency was 33%.

EXAMPLE VIII

Example I was repeated, using 2-methyl-2-nitrosopentane-2-one [prepared] by the method of Harries et al. (Berichte, vol. 3, 1898, pp. 1399 and 1808). The observed NO filtration efficiency was 59%.

EXAMPLE IX

2, 6-dimethyl-6-nitrosohept-2-en-4-one was prepared by treating 4-oxo-tetramethyl-piperidino-1-oxyl bromide with a mixture of aqueous sodium hydroxide and carbon tetrachloride. Example I was again repeated, using the C-nitroso compound thus obtained. The observed NO filtration efficiency was 55%.

EXAMPLE X

Example I was repeated, using N, N-dimethyl-4-nitrosoaniline, sold by the Aldrich Chemical Co. Ltd. The observed NO filtration efficiency was 20%.

The NO filtration efficiency obtained by using the product of example X was low. This is due to the fact that that the N, N-dimethylamino group present in the molecular structure of the C-nitroso compound has an adverse effect on the integrity of the nitroso group. However, as indicated above, in some cases, an NO filtration efficiency as low as 20% could be acceptable. Moreover, the material could be used in association with filter ventilation. One way of realizing such ventilation is indicated below, in example XIII.

EXAMPLE XI

Nitrosobenzene in variable amounts was adsorbed onto a number of activated granular carbons and the respective NO filtration efficiencies were determined as in example I, but using cigarette rods having blended tobacco fillers. The results obtained are shown in table 1 below.

TABLE 1

	Loading					
Carbon	0	2	5	7	10	15
	NO filtration efficiency (%)					
B.P.L.	5	33	47	48	50	55
Anthrasorb CC 1236	0	25	38	39	41	47
MF3	0	11	29	29	32	38
Actibon X	2	23	34	33	38	37
Picatif 60143	8	20	30	36	37	36
207C	7	23	33	39	44	43

B.P.L. and Anthrasorb CC 1236 are anthracite carbons. The first is sold by Pittsburgh Activated Carbon Co., Pennsylvania (United States). MF3, Picatif 60143, and 207C are coconut based carbons sold respectively by Chemviron Ltd., Brussels (Belgium), Pica, Paris (France), and Sutcliffe-Speakman Ltd., Leigh, Lancashire (England). Actibon X is a wood carbon sold by Hooker-Mexicana S. A., Mexico.

Examination of the above table shows that when the nitrosobenzene loading rises from 0 to 5%, the NO filtration efficiency, for all carbons, increases rapidly. However, when the loading levels increase further, up to 15%, the NO filtration efficiency increases more gradually. These results demonstrate that an optimum loading is realized in the 5 to 7% range.

EXAMPLE XII

Example I was repeated, using nitrosobenzene at a 5% loading level on Anthrasorb CC 1844 granular activated carbon. The cigarette rod had a blended tobacco filler. The observed NO filtration efficiency was 53%.

EXAMPLE XIII

Nitrosobenzene was adsorbed at a loading level of 5% onto B.P.L. granular activated carbon. One hundred milligrams of treated carbon was placed in cavity 1 of each of triple filters 2, having, at each end of cavity 1, cellulose acetate filter plug 3, as shown in the single drawing attached, which is a longitudinal cross-sectional diagram of a filter. Each filter, enclosed in porous envelope 4, is attached to cigarette rod 5, having a blended tobacco filler inside envelope 6. Filters 2, which are identical, were attached to corresponding rods 5, by means of tippings 7 having a variable number of rows of micro-perforations 8

realized by laser means, and arranged around a central region of cavity 1 to produce different degrees of ventilation.

The filter cigarettes thus formed, as well as control cigarettes having similar emissions, were smoked under standard conditions until an 8 mm stub was left, and the NO emission for each cigarette was then determined. The control cigarettes differed from the cigarettes described above in that their filter cavities contained 100 mg of untreated B.P.L. activated granular carbon.

The results are shown in Table 2 below.

TABLE 2

Ventilation (%)	untreated BPL carbon		BPL impregnated with 5% nitrosobenzene		Retention due to nitrosobenzene (%)	Expected retention due to nitrosobenzene (%)
	Emission (μg/cig)	Reduction due to ventilation (%)	Emission (μg/cig)	Total reduction (%) due to ventilation + nitrosobenzene		
0	210	-	123	41	41	42
23	148	30	74	65	50	46
43	118	44	41	80	65	48
58	88	58	21	90	76	50
59	77	63	19	91	75	51

The expected NO retention values due to the nitrosobenzene were derived from the relationship between retention and NO emission, which was determined by attaching unventilated triple filters, each of which contained 100 mg of B.P.L. granular activated carbon with a 5% nitrosobenzene loading, to cigarette rods having different, predetermined, NO emissions. We found that the relationship was practically a straight-line relationship.

A comparison of the actual and expected values of NO retention shows that when ventilation increases, the effective retention is increasingly higher than the expected retention, that is, we obtain a synergistic effect.

A similar synergistic effect for NO retention was observed when the ventilation perforations were placed over the cellulose acetate plug end instead of over the cavities. When the perforations were placed over the tobacco end plugs, the synergy was less pronounced.

EXAMPLE XIV

B.P.L. granulated activated carbons having copper loading levels of 0, 0.1%, 1%, 5%, and 10%, were impregnated with nitrosobenzene at loading levels of 0%, 1%, 2%, 5%, 10%, and 15% on a metallized carbon basis.

Hundred milligram doses of the respective carbons were arranged in the cavities of triple filters, each filter comprising, at each end of the cavity, a cellulose acetate plug 5 mm in length. The filters were attached to cigarette rods having a blended tobacco filler. Each cigarette rod was such that it produced an NO emission of approximately 200 μg when no filter was attached. The filter cigarettes thus formed were smoked under standard conditions. In each case, the NO filtration effectiveness of the filter was determined. The results obtained are shown in table 3 below.

TABLE 3

	Copper loading (%)				
	0	0.1	1.0	5.0	10.0
Nitrosobenzene loading (%)	NO filtration effectiveness (%)				
0	< 10	< 10	< 10	< 10	< 10
1.0	17	25	37	33	26
2.0	36	40	48	48	41
5.0	42	46	62.5	65	54.5
10.0	43	56.5	65	61	54
15.0	47	58	67.5	67	53

Table 3 shows that even a copper loading level as low as 0.1% improves the NO filtration effectiveness at all levels of nitrosobenzene loading. A copper loading level of 1% results in an even more significant increase in NO filtration effectiveness. An increase to 5% of the copper loading level only results in an increase of filtration effectiveness very similar to that obtained with a 1% load. An increase to 10% results in an NO filtration effectiveness less than that obtained with loadings between 1 and 5%, and for higher nitrosobenzene loads, the NO filtration effectiveness is even lower than that obtained with 0.1% copper. It may be deduced, therefore, that when nitrosobenzene is used as a C-nitroso compound

and when B.P.L. is selected as the activated carbon, the best copper loading levels are comprised between approximately 1% and approximately 5%. We also observe that for a given copper loading level, the NO filtration effectiveness rises in stages with an increase in the nitrosobenzene loading level from 0 to 2%, but there is relatively little increase in NO filtration effectiveness when the levels of nitrosobenzene loading rise from 5 to 10% and from 10 to 15%. Therefore, there is no apparent advantage in using nitrosobenzene loading levels above approximately 5%, in particular when the copper loading level is comprised between approximately 1 and 5%.

EXAMPLE XV

The procedure of example XIV was used, except that iron loaded activated carbons were used, said carbons being of the B.P.L. type. The results obtained with iron loaded carbons are shown in table 4 below.

TABLE 4

	Iron loading (%)				
	0	0.1	1.0	5.0	10.0
Nitrosobenzene loading (%)	NO filtration effectiveness (%)				
0	< 10	< 10	< 10	< 10	< 10
1.0	17	21	26	25	25
2.0	36	30	41	37	40
5.0	42	40	50	48	44
10.0	43	45	58	50	42
15.0	47	52	61	54	51

As shown in table 4, the overall result is similar to that obtained by using copper loaded carbons, although the increase in NO filtration effectiveness per iron-metallized carbon is not as pronounced as is the case with copper metallization. However, the results do show definite utility, especially when the relatively low cost of iron-loaded carbons is taken into account. Table 4 also shows that the NO filtration effectiveness at a 5% iron loading level does not resemble that for filtration at a 1% loading level, as is

the case with copper-loaded carbons, but is slightly lower. It can therefore be concluded that with B.P.L. carbons treated with nitrosobenzene, the best iron loading levels are close to 1%.

Although in the above examples, the C-nitroso treated carbons were deposited in the triple filter cavities, they can of course be otherwise incorporated in cigarette filters. For example, a C-nitroso treated carbon could be dispersed throughout the cellulose acetate plug or in another fibrous material.

Filter ventilation, as described in example XIII for example, can also be used together with filters in accordance with any of the above examples.

Claims

1. Filter or filtering material to eliminate nitric oxide, especially when contained in tobacco smoke, comprising activated carbon, and characterized in that a C-nitroso compound is adsorbed on this carbon, one (or more) substituent groups of this compound, other than the nitroso group or groups, being of such identity and position in the molecular structure of said compound that it has no adverse or dangerously harmful effect on the integrity of the nitroso group or groups.

2. Filter or filtration material according to claim 1, characterized in that the C-nitroso compound is an aromatic compound.

3. Filter or filtration material according to claim 2, characterized in that the C-nitroso compound is nitrosobenzene.

4. Filter or filtration material according to claim 2, characterized in that the C-nitroso compound is 2-nitrosotoluene.

5. Filter or filtration material according to claim 2, characterized in that the C-nitroso compound is 2, 4, 6-trimethylnitrosobenzene.

6. Filter or filtration material according to any of claims 1 to 5, characterized in that the activated carbon, preferably a coal-based carbon, has a particulate form.

7. Filter or filtration material according to any of claims 1 to 6, characterized in that the activated carbon has been loaded with a metal, for example, copper or iron, and preferably at a loading level in the range of 0.1% to 5% by weight on an untreated carbon basis.

8. Filter or filtration material according to any of claims 1 to 7, characterized in that the loading level of the C-nitroso compound is in the range 2 to 15%, and preferably 2 to 7% by weight on an untreated carbon basis.

9. Filter according to any of claims 1 to 8, characterized by a ventilation device intended to draw air into the filter.

10. Process for filtering nitric oxide in a gaseous medium, characterized in that this medium is placed in contact with a filtration material according to any of claims 1 to 8.

[One drawing follows.]